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HIGH-RIGIDITY SLIDING MATERIAL [Kogosei Setsudo Zairyo]

Isamu Kobayashi et al.

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INVENTOR(S)	(72):	Isamu Kobayashi et al.
APPLICANT(S)	(71):	Kubota Tekko K.K.
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## Specification

# Title of the invention High-Rigidity Sliding Material

### 2. Claim

A high-rigidity sliding material, characterized by the fact that titania fibers are mixed in a synthetic resin.

# Detailed explanation of the invention (Industrial application field)

The present invention pertains to a high-rigidity sliding material that requires both characteristics of a high rigidity and sliding characteristics.

(Prior art)

As high-rigidity sliding materials that require a high

As high-rigidity sliding materials that require a high rigidity and a low fraction characteristic during sliding, for example, gears and bearings themselves or housing for integrating bearings, etc., fiber-reinforced composite materials in which various kinds of reinforcing fibers are mixed with a synthetic resin as a matrix are broadly used.

<sup>&</sup>lt;sup>1</sup> Numbers in the margin indicate pagination in the foreign text.

Then, as one of reinforcing materials for these composite materials, potassium hexatitanate fibers and glass fibers are known.

However, in the conventional fiber-reinforced composite materials that have been used as high-rigidity sliding materials, there are the following problems, and it is difficult to say that the composite materials up to now always have optimum characteristics as high-rigidity sliding materials in actuality.

In other words, for example, in a composite material in which potassium hexatitanate fibers are mixed as a reinforcing material, if the other party material during sliding is a hard metal material such as iron and steel products and Al product, the coefficient of kinetic friction is high, and the amount being woven is increased in both the hard metal material and the other party. Also, in a composite material in which glass fibers are mixed as a reinforcing material, the coefficient of kinetic friction is higher than that of the above-mentioned composite material, although its amount being worn is decreased, so that the other party material is worn out much. Furthermore, in a composite material in which the above-mentioned potassium hexatitanate fibers are mixed, the sliding characteristics are more inferior to those of the

above-mentioned glass fiber-reinforced composite material in accordance with the kind of synthetic resin being a matrix.

(Problems to be solved by the invention)

The present invention solves these technical problems, and its purpose is to provide a high-rigidity sliding material in which the coefficient of kinetic friction is low and the amount being worn can be reduced as much as possible in both the sliding material and the other /2 party being.

(Means to solve the problems)

In order to achieve the above-mentioned purpose, the essence of the high-rigidity sliding material of the present invention is characterized by the fact that titania fibers are mixed in a synthetic resin.

(Operation)

These inventors since the characteristics of the fiber-reinforced composite materials depend on the characteristics of the reinforcing fibers, the characteristics of the conventional reinforcing materials reviewed. As a result, in case potassium hexatitanate fibers are used as the reinforcing material, since the mohs hardness of said fibers is as relatively low as 4, when the other party material has a hard hardness like a metal

material, it is simply worn out, and a large amount of worn powder is generated, though they are fine powders, so that a rough worn-out state is formed. Thereby, the amount being worn in the other party is also increased. Also, in case glass fibers are used as the reinforcing material, the mohs hardness of said fibers is as relatively high as 6, and the glass fibers themselves are difficult to be worn out, however since the fiber diameter is thick, relatively large worn-out powders are generated, and when sliding, a rough worn-out state in which an abrasive is sandwiched is formed.

Accordingly, these inventors considered that if fibers with appropriate hardness and diameter were mixed as a reinforcing material, a desired fiber-reinforced composite material could be obtained and repeated various reviews.

As a result, it was discovered that titania fibers (titanium oxide fibers) were reinforcing materials that met the above-mentioned requirements. In other words, in a fiber-reinforced composite material in which the titania fibers are used as a reinforcing material, when it is used as a sliding material, the coefficient of kinetic friction is decreased, so that the amount being worn is reduced in the composite material and the other party material and the temperature rise due to the frictional heat is also

decreased. In other words, since the diameter of the titania fibers is about the same as that of the abovementioned potassium titanate fibers and their mohs hardness is 5, the powders being worn out are reduced, and the amount being worn out is also reduced, so that the sliding resistance (coefficient of kinetic friction) is decreased. In addition, since the elastic modulus of the titania fibers is twice of the above-mentioned potassium hexatitanate and 8 times of the glass fibers, the fiberreinforced composite material exhibits a high rigidity when the titanate fibers are used as a reinforcing material. Furthermore, since the titania fibers have a fine fiber diameter that is about the same as that of the potassium titanate fibers, the dispersibility into the matrix is improved, so that the anisotropy in the properties of the composite material being obtained is reduced, the warp is little, and the surface is smooth.

Also, the titania fibers being used in the present invention is obtained heating and dehydrating hydrated titanic acid fibers at several hundreds °C or higher and can also be easily obtained by oxidizing with an air in a chloride molten salt containing titanium tetrachloride.

Also, it has already been known that the hydrated titanic acid fibers are obtained by a method that hydrothermally

acicular alkali titanate (generally, potassium tetratitanate fibers being obtained by a baking method or flux method) with water or an acid solution and removes the alkali (Yanagida and Shimizu, Journal of Fiber Society, 34 (1978), 319), a method that treats a plate-shaped alkali titanate (generally, potassium dititanate fibers obtained by a melt method) with an acid aqueous solution and removes the alkali (Fujiki and Osaka, Journal of Ceramic Association, 90 (1982), 19), or a method that oxidizes an aqueous titanium trichloride solution with an air (Powder Metallurgy Association, 1980 Fall Convention Lecture Summary 2-6, p.86).

Since the mixture ratio of the titanate fibers depends on the kind of synthetic resin being a matrix, it is not limited at all, however the ratio is preferably about 5-50 wt%. Furthermore, the kind of synthetic resin being used as a matrix is not limited at all, and for example, thermoplastic resins such as polyamide resin, polyacetal resin, polycarbonate resin, polybutylene terephthalate resin, polyphenylene sulfide resin, polyethylene terephthalate resin, polyphenylene resin, and polyether sulfone resin or thermosetting resins such as phenol resin, epoxy resin,

unsaturated polyester resin, and urethane resin are mentioned.

Also, with the use of a sliding enhancer (fluororesin powder, silicone, silicon powder, polyethylene, mineral oil, molybdenum disulfide, etc.) in combination is preferable in further improving the sliding characteristics of the sliding material of the present invention.

Next, the present invention is explained in further detail by application examples, however the following /3 application examples do not limit the present invention. Any design change through the above-mentioned essence is included in the technical range of the present invention. (Application examples)

Next, titania fibers were manufactured by the following process.

- (I) Preparation of raw materials
- (1) Titanium compound: natural rutile sand (produced in Australia)

#### <Component> (wt%)

 $TiO_2$ : 95.6%,  $Fe_2O_3$ : 0.6%, P: 0.01%, S: 0.02%,  $ZrO_2$ : 0.7%,  $Cr_2O_3$ : 0.3%,  $SiO_2$ : 0.6%,  $V_2O_5$ : 0.7%,  $Nb_2O_3$ : 0.3%,  $Al_2O_3$ : 0.4%, MnO: 0.01%, CaO: 0.03%, MgO: 0.03%, and the balance: an infinitesimal amount of Co, Ca, etc.

(2) Potassium compound: K<sub>2</sub>CO<sub>3</sub> (purity: 99.5%)

(3)  $TiO_2/K_2O$  (mol ratio): 2.0

# (II) Heating melting

A raw material mixed powder was put into a platinum crucible and heated at  $1,100^{\circ}\text{C}$  for 40 min.

# (III) Rapid cooling treatment

The melted product was flown down to a metal twin roll being rotated at high speed, so that a solidified product with a foil segment shape was obtained.

It was confirmed from an X-ray diffraction that the solidified product was amorphous.

## (IV) Baking treatment

The above-mentioned natural rutile sand was mixed with the above-mentioned amorphous solidified product at a mol ratio of  $TiO_2/K_2O$  of 3.0 and pulverized by a disk mill, so that a uniform powder mixture (average particle size: 5  $\mu$ m) was attained. Next, the powder mixture was charged into an aluminum crucible, heated at 1,000°C for 0.5 h and held.

The above-mentioned baked product was charged into water at an amount of 10 times (weight ratio), and the fibers were shredded for 15 min by a mixer, dehydrated, and dried, so that potassium tetratitanate fibers were obtained. Its diameter was 0.2-1  $\mu$ m, and its length was 5-20  $\mu$ m.

#### (V) Potassium removal treatment

The potassium tetratitanate fibers obtained in this manner was immersed into an aqueous sulfuric acid solution (5 %) as a washing solution (1 g fibers/10 cc washing solution), and K<sup>+</sup> ions were eluted for about 60 min. Then, the fibers were washed with water and dried.

### (IV) Baking treatment

The fibers from which the potassium was removed was put into an aluminum crucible, charged into a furnace set at  $400^{\circ}\text{C}$ , and baked for about 0.5 h.

As a result of its X-ray analysis, it was shown that the fibers obtained were titania fibers (anatase phase). Also, the fiber shape was 0.1-1  $\mu m$  in diameter and 5-20  $\mu m$  in length.

As a matrix, nylon 66 (Ny66), polybutylene terephthalate (PBT), polyacetal (POM), polyphenylene sulfide (PPS), or a resin in which polyethylene (PE) is mixed with Ny66 were used, and the above-mentioned titania fibers (application example) and the potassium hexatitanate or glass fibers (comparative example) were mixed with the above-mentioned matrix at ratios shown in the following Table 1, so that various kinds of fiber-reinforced composite materials were manufactured. For each composite material obtained, the specific gravity, the tensile

strength, and the bending elastic modulus were respectively measured according to ASTM D792, ASTM D638, and ASTM D790, and the sliding performances were investigated by a Suzuki type wear test (stress  $P = 10 \text{ kgf/cm}^2$ , speed V = 30 cm/sec). Also, for the sliding performances, a S45C stainless steel with a surface roughness (Ra) of 0.50 was used as the other party material, and after rotating and sliding said other party material for 1 h, the value was attained.

The results are also show in Table 1, and for the specific gravity, the tensile strength, and the bending elastic modulus in Table 1, the absolute values of the mixture with Ny66 as a matrix are shown.

Table 1

/4

Na.	. 私 会 利 会 (115%)	lt A	引 波 り 弦 さ (kg[/cu²)	部印塑性 係数 (kgf/cm²)	据 脏 特 按				
					验净物质数	turf(ii (sa²/kgf·ha)	相手材比認托旗 (au <sup>3</sup> /kgf·ko)	対の報告の対象は	一件 考
1	Ny88:70,チタニア採稿:30	1.41	1400	110500	0.26	0.34	0.002	56	実施例
2	My58:70, 8生タン酸カリウム構造   :30	1.47	1323	\$5000	3.40	0.55	0.00%	15	比較例
3	Vy66:70,ガラス退後:30	1.36	1750	ecot 6	a, to	6.38	0.810	<b>9</b> :1	н
4	PBT:70. チタニア開経:30	1.59	1630	105000	0.25	D. 15	ien.c	5.2	実統例
5	プラ7:70.5チタン酸カリウム繊維:30	1.11	1030	93005	6.19	0.20	G. 901	13	12.62.55
6	PBT:70. ルラス版地:10	1.52	1320	90000	0.56	0.16	0.917	#6	.,,
7	PD41:80、子·タニ77基種:20	1.58	350	75000	0.30	0.47	0,000	£0	灾族例
fl.	POM: 80.8チタン酸カリウム繊維: 16	1.59	839	62000	9.13	0.65	0.303	80	2012/00
9	PON:80、ガラス総額:20	2.54	900	65000	0.70	1.82	0.015	162	#
10	PPS:60. 子夕二71届和:(0	1.76	1350	155600	6.28	81.18	0.261		沙塘倒
11	PP5:66.6チタン酸カリウン酸粒:40	1 79	1350	140000	0.37	0.80	0.102	50 %	HERRY
12	PP5:60、ガラス繊維: 09	1.56	3720	125000	0.58	0.45	0.412	90	IJ
13	HyE8:63:PE:7。チタニア科粒:30	1,38	1210	93000	0.11	0.15	0.001	47	现象例
14	My66:63 JE:7 Jチタン酸カリウム線	1.35	1250	88080	3.16	80.9	0.077		比較份
15	部:36 Ny65:63.7E:7。ガラス機能:30	7.34	1560	75กจอ	0.25	0.07	8.002	56	,,

- 1. Mixture ratio (wt%)
- 2. Specific gravity
- 3. Tensile strength (kgf/cm<sup>2</sup>)
- 4. Bending elastic modulus (kgf/cm<sup>2</sup>)
- 5. Sliding characteristics
- 6. Remarks
- 7. Coefficient of kinetic friction
- 8. Relative amount of wear  $(mm^3/kgf \cdot km)$
- 9. Relative amount of wear of the other party material  $(mm^3/kgf\cdot km) \label{eq:material}$
- 10. Sliding surface resin temperature (°C)
- 11. Ny66: 70, titania fibers: 30

Ny66: 70, potassium hexatitanate fibers: 30

Ny66: 70, glass fibers: 30

12. Ny66: 70, titania fibers: 30

Ny66: 70, potassium hexatitanate fibers: 30

Ny66: 70, glass fibers: 30

13. POM: 80, titania fibers: 20

POM: 80, potassium hexatitanate fibers: 20

POM: 80, glass fibers: 20

14. PPS: 60, titania fibers: 40

PPS: 60, potassium hexatitanate fibers: 40

PPS: 60, glass fibers: 40

15. Ny66: 63, PE: 7, titania fibers: 30

Ny66: 63, PE: 7, potassium hexatitanate fibers: 30

Ny66: 63, PE: 7, glass fibers: 30

16. Application example

Comparative example

Ny66: A-3W made by Mitsubishi Yuka Badische Co., Ltd.

PBT: Juranex 2002 made by Polyplastics Co., Ltd.

POM: Jurakon M-90 made by Polyplastics Co., Ltd.

PPS: Photron Powder made by Kureha Chemical Industry Co.,

Ltd.

PE: Ryumal 5000 Powder made by Mitsui Petrochemical Industries, Ltd.

Potassium hexatitanate fibers: Dismo D made by Otsuka Chemical Co., Ltd.

Glass fibers: Chopped Strand with a diameter of 11  $\mu m$  and a length of 3 mm made by Nippon Glass Fibers K.K.

As seen from the results of Table 1, it is understood that since the fiber-reinforced composite materials (application examples) using the titania fibers as a reinforcing material have a low coefficient of kinetic friction, the amount of wear in the composite materials and the other party material is small. Also, as seen from the comparison of the characteristics by changing the

reinforcing material while commonly using the matrix, the composite materials in which the titania fiber is mixed have a rigidity higher than that of the composite materials in which the potassium hexatitanate or glass fibers are mixed.

(Effects of the invention)

As mentioned above, according to the present invention, with the formation of the composite material by using titania fibers as a reinforcing material, a high-rigidity sliding material in which the coefficient of kinetic friction is low and the amount of wear is reduced as much as possible in the sliding material and the other party material can be realized.